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2012 J. Phys.: Condens. Matter 24 375601

(http://iopscience.iop.org/0953-8984/24/37/375601)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **24** (2012) 375601 (8pp) doi:10.1088/0953-8984/24/37/375601

Magnetic excitations in $EuCu_2(Si_xGe_{1-x})_2$: from mixed valence towards magnetism

P A Alekseev[1,2], **K S Nemkovski**[3], **J-M Mignot**[4], **V N Lazukov**[1], **A A Nikonov**[1], **A P Menushenkov**[2], **A A Yaroslavtsev**[1,2], **R I Bewley**[5], **J R Stewart**[5] and **A V Gribanov**[6]

[1] National Research Centre 'Kurchatov Institute', 123182 Kurchatov sqr. 1, Moscow, Russia
[2] National Research Nuclear University 'MEPhI', Kashirskoe shosse 31, 115409, Moscow, Russia
[3] Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science, Außenstelle am FRM II, Lichtenbergstraße 1, 85747 Garching, Germany
[4] Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif sur Yvette, France
[5] ISIS Pulsed Neutron and Muon Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK
[6] Chemistry Department of the Moscow State University, Leninskie Gory, GSP-1, 119991 Moscow, Russia

E-mail: k.nemkovskiy@fz-juelich.de

Received 5 April 2012, in final form 2 August 2012
Published 23 August 2012
Online at stacks.iop.org/JPhysCM/24/375601

Abstract

We report the inelastic neutron scattering study of spin dynamics in $EuCu_2(Si_xGe_{1-x})_2$ ($x = 1, 0.9, 0.75, 0.6$), performed in a wide temperature range. At $x = 1$ the magnetic excitation spectrum was found to be represented by the double-peak structure well below the energy range of the Eu^{3+} spin–orbit (SO) excitation $^7F_0 \rightarrow ^7F_1$, so that at least the high-energy spectral component can be assigned to the renormalized SO transition. Change of the Eu valence towards 2+ with increased temperature and/or Ge concentration results in further renormalization (lowering the energy) and gradual suppression of both inelastic peaks in the spectrum, along with developing sizeable quasielastic signal. The origin of the spectral structure and its evolution is discussed in terms of excitonic model for the mixed valence state.

(Some figures may appear in colour only in the online journal)

1. Introduction

Instabilities affecting the charge or spin degrees of freedom of inner f-electron shells in lanthanide and actinide compounds are central to a wide range of fascinating phenomena discovered in those systems, such as 'heavy-fermion (HF) superconductivity', non-Fermi liquid states, Kondo insulators, etc. Interesting physics typically occurs at low temperature in the regime where long-range magnetic order becomes destabilized either spontaneously, or by means of an external control parameter (pressure, magnetic field, compositional tuning, etc). In the case of rare earths, most experimental and theoretical effort has been focused on the Ce and Yb elements, but valence (i.e. charge) instabilities are also prone to occur near the middle of the lanthanide series, and have indeed been reported for a number of Sm- and Eu-based materials.

Detailed inelastic neutron scattering (INS) studies of the intermediate valence (IV) Sm compounds (Sm, Y)S [1–4] and SmB_6 [5–8], belonging to the class of 'intermediate valence semiconductors', have shed light on their most unusual spin dynamics. Corresponding information for Eu compounds is in high demand, especially since the Eu^{3+} $4f^6$ configuration is identical to that of Sm^{2+} ($^7F_0$ multiplet ground state), and Eu^{2+} ($4f^7$) is a pure spin state ($J = S = 7/2$, $L = 0$). Obviously, our general understanding of spin and charge fluctuations in f electron systems would greatly benefit from an experimental overview encompassing elements not only from the beginning and the end, but also from the

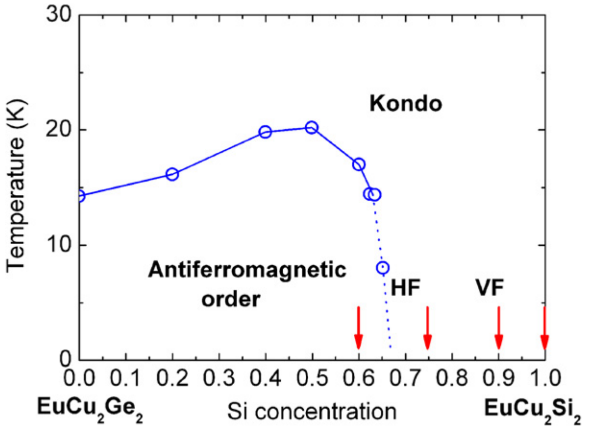

Figure 1. Magnetic phase diagram of EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$, after [13]. 'HF' and 'VF' indicate the regions corresponding to the heavy-fermion and valence-fluctuating regimes, respectively. Arrows indicate the compositions discussed in the text.

middle of the rare-earth series. Extending the investigations to compounds with metallic character would also be worthwhile. On the other hand, since the valence instability is inherent to the most europium-based compounds, proper description of this phenomenon at the microscopic level can be important for the understanding other properties. For instance, recently the evidence of relation between formation of the IV and superconductivity has been reported for EuFe$_2$As$_2$ under applied external and chemical pressure [9]. Unfortunately, the huge neutron absorption cross-section of natural Eu (4530 barn at a neutron energy of 25 meV), combined with the prohibitive cost of less-absorbing isotopes, has strongly hampered the progress of INS experiments on Eu-based materials. Results published to date are limited to a couple of compounds, EuPd$_2$Si$_2$ [10] and EuNi$_2$P$_2$ [11], and the origin of the observed excitations remains unsettled.

The EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$ family was recently shown to be of particular interest [12, 13], because the rare-earth ion configuration changes from nearly integral valence Eu^{2+} (4f^7) in EuCu$_2$Ge$_2$ (magnetically ordered below $T_N = 14$ K, with approximately the full Eu^{2+} magnetic moment) to a valence fluctuating (VF) state above $x \approx 0.6$. One striking feature of the Ge-rich region is the coexistence of the magnetically ordered phase with valence fluctuations, which is quite unusual amongst f electron compounds except for a few examples such as certain thulium chalcogenides [14]. Clear evidence was reported for Kondo anomalies ($-\ln T$ slope in the resistivity, temperature maximum in the thermoelectric power) at Si concentrations $x > 0.5$, as well as for strong electron mass enhancements (linear specific heat coefficient up to 0.3 J K^{-2} mol^{-1} for $x = 0.65$, enhanced Fermi liquid AT^2 term in the resistivity). In EuCu$_2$Si$_2$ and Si-rich solid solutions, the valence exhibits a pronounced temperature variation, gradually becoming more 3+ as temperature goes down. The phase diagram designed for EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$ series [13] is shown in figure 1.

In this paper, we present a detailed INS study of the dynamical magnetic response in EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$ series ($x = 1$, 0.9, 0.75, 0.6). Different spectral components, with pronounced temperature and composition dependences are reported, and their properties are discussed in connection with previous results for Sm IV compounds. Some results for pure EuCu$_2$Si$_2$ have been partly published in conference proceedings [15, 16].

2. Samples and experimental details

Polycrystalline EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$ samples with compositions $x = 1$, 0.9, 0.75, and 0.6 (marked by arrows in the phase diagram in figure 1) have been synthesized at Moscow State University by argon arc melting followed by long-term (about 400 h) homogenization annealing. Seven grams of EuCu$_2$Si$_2$ ($x = 1$) were prepared using the ^{153}Eu isotope. On this enriched sample, good experimental conditions for studying the magnetic spectral response were obtained at an incident neutron energy of $E_i =$ 100 meV with a powder sample thickness of 2.5 mm (85% transmission). However, because of the high cost of rare-earth isotopes, other compositions were synthesized using natural europium. Accordingly, the thickness was reduced to 0.4 mm, corresponding to a total mass of 2 g for the maximum allowable transverse sample dimensions. This yielded a still reasonable transmission of about 70%.

The valence state of europium in EuCu$_2$Si$_2$ is known to be quite sensitive to the sample preparation method and, in some cases, Eu ions were even found to be in a pure divalent state instead of mixed valence [17–20]. Single-crystal specimens were found to be more prone to this problem than powder samples, which usually exhibit a clear intermediate valence (IV), as derived from their lattice constants. A detailed discussion of this problem is given in [19]. On the other hand, for powder samples the characteristic problem is the presence of the so-called satellite phase where europium is nearly divalent [21]. This satellite phase seems to be common for most IV Eu-based systems with ThCr$_2$Si$_2$ structure [11] and typically contains 10–20% of Eu ions in the sample (for more details see [10, 11, 21] and references therein).

The quality of the samples was checked carefully using x-ray diffraction, AC susceptibility, and DC magnetization measurements. X-ray diffraction analysis revealed no impurity phases within the limits of sensitivity. The lattice constants and magnetic susceptibilities obtained were in a good agreement with the literature data for both EuCu$_2$Si$_2$ [22, 23] and the EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$ solid solutions [12, 13, 24]. The fraction of Eu ions contained in the satellite divalent phase was estimated from susceptibility data to be within 5–7% for all samples, confirming the rather high quality of our samples.

X-ray absorption near edge structure (XANES) experiments were carried out on the A1 beamline at the DORIS-III storage ring (DESY, Hamburg, Germany). The measurements were performed in transmission mode above the L$_3$–Eu (6977 eV) absorption edge. The energy resolution of the double-crystal Si(111) monochromator (detuned to 50% rejection of the incident signal in order to minimize harmonic contamination) with a 0.3 mm slit was about 1.2 eV at 7 keV. Low-temperature measurements (8 K $\leq T \leq$ 300 K) were carried out using a liquid–helium continuous-flow cryostat

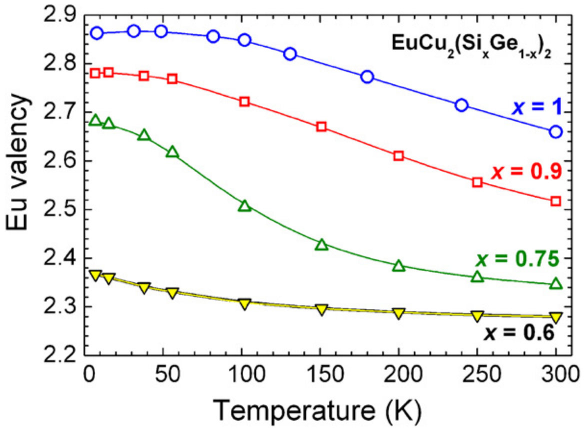

Figure 2. Temperature dependence of the average europium valence in $EuCu_2(Si_xGe_{1-x})_2$ samples, as deduced from XANES measurements.

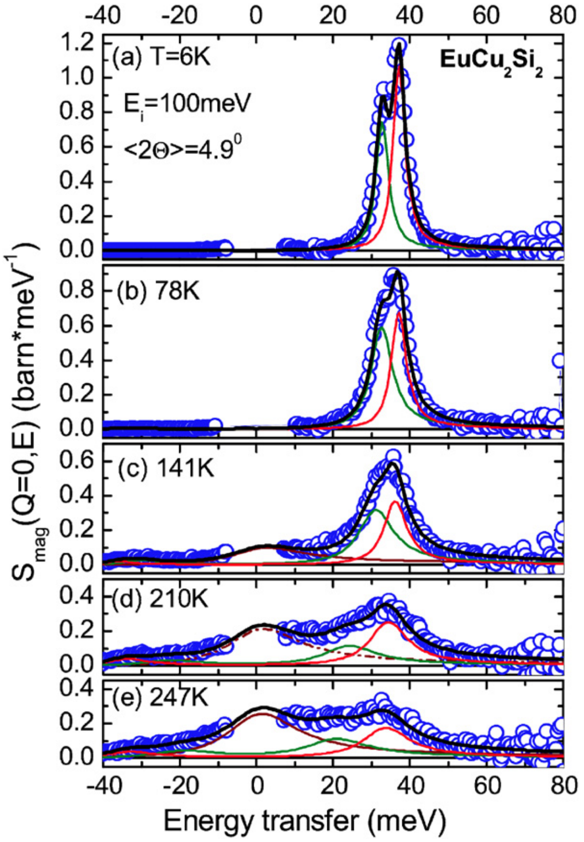

Figure 3. Magnetic excitations in $EuCu_2Si_2$ at different temperatures for average scattering angle $\langle 2\theta \rangle = 4.9°$. Incident neutron energy $E_i = 100$ meV. The spectra have been reduced to $Q = 0$ assuming the magnetic dipole form factor for Eu^{3+} $^7F_0 \rightarrow ^7F_1$ spin–orbit transition. Symbols: experiment, lines: fits using Lorentzian spectral functions (see text).

with a temperature control within ±1 K at 300 K and ±0.1 K at 5 K.

The separation of the spectral components arising from different europium valence states was achieved by fitting (XANDA program [25]) the experimental L_3–Eu XANES spectra, corrected for a polynomial background, to combinations of Lorentzian (representing core-hole lifetime width) and arctangent (describing the transitions to the continuum) curves of constrained widths and energy positions, as was done in [26]. In this approach the amount of Eu ions in each valence state is assumed to be proportional to the area under the corresponding Lorentzian curve or, equivalently, to its weight in the fitting formula [26]. Obviously, the presence of the satellite Eu-divalent valence shifts the average valence deduced from XANES spectra towards lower values. Therefore, all the data have been corrected for the amount of the divalent phase.

The resulting temperature dependence of the Eu valence is summarized in figure 2 for all Si concentrations. The general behaviour is similar to that reported by Fukuda *et al* [24], though absolute values are somewhat higher in our case, possibly reflecting differences in the sample preparation procedures. In addition, the correction for satellite phase may produce some additional discrepancy. One sees that the temperature variation of the valence strongly depends on the composition. It is quite strong for concentrations in the heavy-fermion (HF) and valence-fluctuation (VF) regions of the phase diagram in figure 1, and rather weak in the magnetic region (the sample with $x = 0.60$ has an antiferromagnetic ground state). It is remarkable, however, that, even there, the valence remains distinctly higher than the integral value 2+.

INS experiments have been carried out on the time-of-flight spectrometers HET ($EuCu_2Si_2$) and MARI ($EuCu_2[Si_xGe_{1-x}]_2$) at ISIS/RAL (UK). In all experiments the neutron incident energy was $E_i = 100$ meV. In the case of $EuCu_2(Si_xGe_{1-x})_2$ the instrument resolution was relaxed to 7.1 meV at zero energy transfer by using a lower chopper frequency $\nu = 150$ Hz, as a trade-off to increase the neutron flux. However, several spectra were also recorded with much better energy resolution (3.7 meV at $E = 0$) by doubling the chopper frequency ($\nu = 300$ Hz). The spectra measured were combined into five groups for low scattering angles (3°–29°) and two groups for the scattering angles above 100°. A $LaCu_2Si_2$ specimen was also measured to estimate the nonmagnetic background by means of the standard procedure suggested by Murani [27]. Absolute calibration of the spectral data was achieved by normalization to a vanadium standard. Absorption corrections to the spectral function were calculated for a flat sample geometry, and multiple-scattering effects were neglected considering the small sample thickness and the high absorption within the sample plane.

3. Experimental results

3.1. $EuCu_2Si_2$

The magnetic excitation spectra measured for $EuCu_2Si_2$ are shown in figure 3 for different temperatures. At $T = 6$ K (upper frame), the europium valence is close to 3+ state, but no excitation is observed at the energy of 46 meV where the $^7F_0 \rightarrow ^7F_1$ spin–orbit (SO) transition of Eu^{3+} is expected to occur[7] [28]. Instead, the dynamical magnetic

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[7] The present experimental conditions, with higher incoming neutron energies, provide a more favourable kinematic factor in the energy range of interest for observing this Eu^{3+} SO excitation than those used in [10, 11].

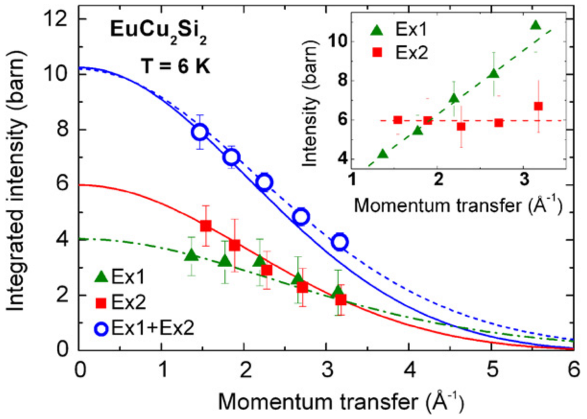

Figure 4. Integrated intensities of Ex1 (triangles) and Ex2 (squares) and total inelastic intensity (circles) in $EuCu_2Si_2$ at $T = 6$ K as a function of momentum transfer. Solid lines represent the squared magnetic form factor for the $^7F_0 \rightarrow {}^7F_1$ Eu^{3+} transition, normalized to the intensity of Ex2, or the total inelastic intensity, at the minimum experimental Q value. Dash-dotted line: $\langle j_0 \rangle^2(Q)$ normalized to the intensity of Ex1 at the minimum experimental Q value. Dotted line: calculated form factor for the total inelastic intensity. Inset: intensities of Ex1 and Ex2 obtained by fitting the spectra measured at different scattering angles and reduced to $Q = 0$ using the form factor for the $^7F_0 \rightarrow {}^7F_1$ Eu^{3+} transition; dashed lines—guides for the eye.

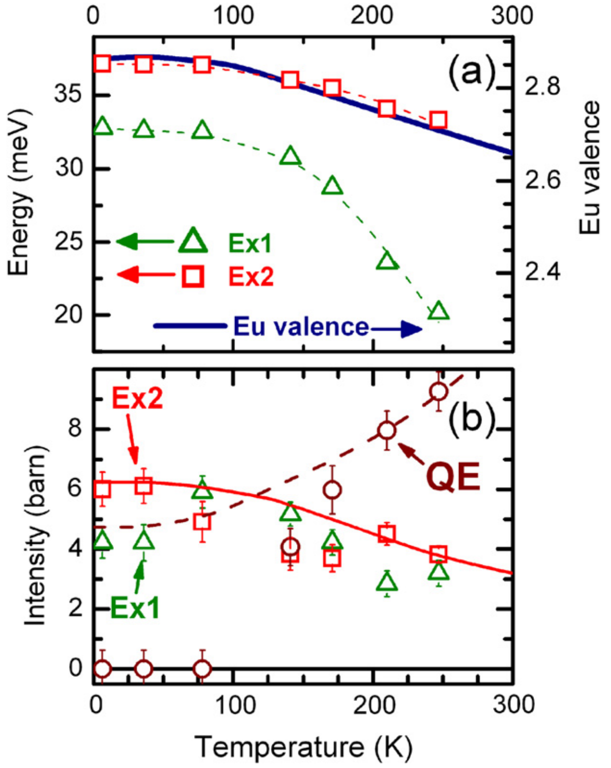

Figure 5. Temperature dependences of the energies (a) and integrated intensities (b) of the inelastic peaks Ex1 and Ex2, and the quasielastic peak. Solid line in (a): temperature dependence of the Eu valence in $EuCu_2Si_2$, dashed lines in (a): guides to the eye. Lines in (b): calculations (see text).

response exhibits two pronounced peaks at 32.5 and 37 meV (hereafter denoted Ex1 and Ex2, respectively). A careful analysis indicates that the integrated intensities of Ex1 and Ex2 have different dependences on the momentum transfer Q (figure 4). Ex2 follows the magnetic dipole form factor calculated for the $^7F_0 \rightarrow {}^7F_1$ transition, but in the case of Ex1 the intensity decreases more slowly. To illustrate this effect the experimental spectra measured at different scattering angles were reduced to $Q = 0$ using the above form factor. With this correction made (inset in figure 4), the intensity of Ex2 becomes independent on Q, whereas that of Ex1 *increases* with Q, reflecting the deviation of the real form factor from that of the $^7F_0 \rightarrow {}^7F_1$ transition. The dash-dotted line in figure 4 represents the extrapolation of this form factor to $Q = 0$.

It is worth noting, in this connection, that since the peaks observed in $EuCu_2Si_2$ spectra are broader than instrumental resolution and have nearly Lorentzian shapes, correction for the form factor is important for the proper fitting of the peak wings, especially at high temperatures where the peaks became broader and considerable quasielastic (QE) signal appears[8] (see below). The exact dependence of the form factor for Ex1 outside the range 1.5–3.5 $Å^{-1}$ is not known, and there is no reliable experimental information as to the form factor of the QE peak. Therefore, the analysis of the temperature evolution (figures 3 and 5) was performed using only data from the lowest scattering angle bank ($2\theta = 3°–7°$), in which the effect of the form factor variation is minimized because of low momentum transfer values. For simplicity, the same form factor as for the $^7F_0 \rightarrow {}^7F_1$ transition was thus assumed, neglecting deviations in Q-dependences for Ex1 and (possibly) for the QE signal.

Increasing temperature gives rise to a gradual broadening and intensity reduction of both Ex1 and Ex2, while shifting their positions towards lower energies. This indicates the influence of the f-shell population (degree of IV) on the excitation spectra in $EuCu_2Si_2$. The shift with temperature in the energy position of Ex2 is seen to follow the temperature evolution of the Eu valence (figure 5(a)). The decrease in the energy of Ex1 is much steeper, especially above $T^* \sim 100$ K. The decrease in the integrated intensity of Ex2 with increasing temperature (figure 5(b)) can be accounted for using the temperature dependence expected from thermal population effects on the $^7F_0 \rightarrow {}^7F_1$ SO transition, corrected for the change in the Eu^{3+} fraction. For Ex1, the integrated intensity can be regarded as constant within experimental accuracy.

A remarkable feature of the $EuCu_2Si_2$ magnetic spectra is the absence of detectable QE signal in the low-temperature response. Namely, Eu^{2+} has a pure spin 4f configuration ($L = 0$, $J = S = 7/2$), and the only contribution to the INS spectra in zero magnetic field can be QE scattering[9]. With a calculated magnetic cross-section of 38.5 barn such a contribution should be visible, even for a relatively low 'fraction' of Eu^{2+}, estimated from the average valence (see figure 2) to be about

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[8] In spectra measured at fixed scattering angle, the momentum transfer changes as a function of energy, and this effect becomes significant even for fitting a single peak if its energy width is large.

[9] No CF effect is expected, in the first approximation, for the ground state multiplet $J = 7/2$ multiplet with $L = 0$.

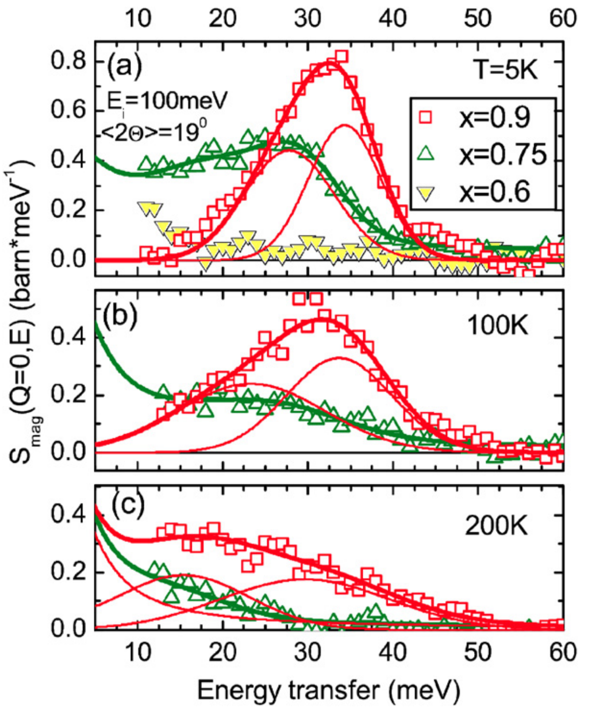

Figure 6. Magnetic excitations in $EuCu_2(Si_xGe_{1-x})_2$ reduced to $Q = 0$ according to the magnetic form factor for the $^7F_0 \rightarrow ^7F_1$ Eu^{3+} spin–orbit transition. Incident neutron energy $E_i = 100$ meV. Average scattering angle $\langle 2\theta \rangle = 19°$. Symbols: experiment; thick lines: fitting to the experimental spectra, thin lines: partial spectral components for $x = 0.9$.

15% at $T = 10$ K. The corresponding spectral intensity should be comparable with those of Ex1 or Ex2. In the measured spectra, the QE signal appears only at temperatures above $T^* \sim 100$ K, then it rapidly recovers the intensity expected from the partial Eu^{2+} fraction, represented by the dashed line in figure 5(b). The QE peak is rather broad, with a full width at half maximum (FWHM) of about 22 meV at 100 K, and its width remains nearly constant, within experimental accuracy, in the whole temperature range above 100 K. Interestingly, T^* approximately coincides with the temperature at which the Eu valence and the energies of both Ex1 and Ex2 start to deviate from their values measured at 6 K.

3.2. $EuCu_2(Si_xGe_{1-x})_2$ solid solutions

The substitution of Si by Ge produces a decrease in the Eu valence and results in a further evolution of the dynamical magnetic response in $EuCu_2(Si_xGe_{1-x})_2$ (see figure 6). This is evidenced by a decrease in the energies of the inelastic peaks, qualitatively similar to the effect of increasing temperature. Meanwhile, the contribution of the quasielastic scattering becomes more significant. At the lowest Ge concentration ($x = 0.9$) the low-temperature spectrum (figure 6(a)) consists of two peaks at energies of 27 and 34 meV. It is natural to identify them with Ex1 and Ex2, respectively. One can see that the widths are much larger than for $x = 1$. This broadening cannot be due to the different measuring conditions on MARI (section 2), since a test performed with two times better energy resolution produced no significant change. As with undoped $EuCu_2Si_2$ the energies and integrated intensities of Ex1 and Ex2 decrease with increasing temperature. Although the broadening and the shift to lower energies of the inelastic peaks hampers the unambiguous detection of the QE peak, it is reliably detected at least at $T = 200$ K.

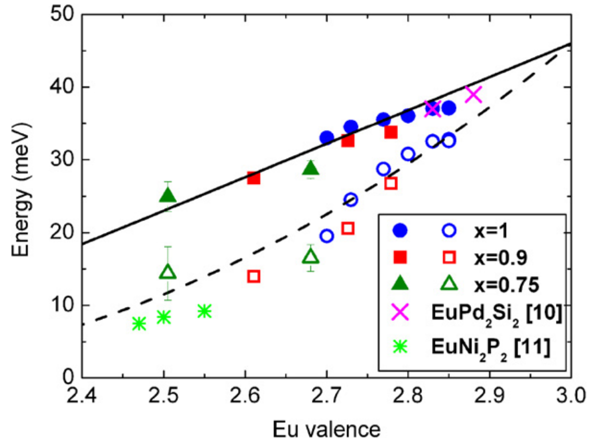

Figure 7. Dependence on the Eu valence of the energies of Ex1 and Ex2 in $EuCu_2(Si_xGe_{1-x})_2$. Data points correspond to different compositions (denoted by markers) and temperatures. Lines: model calculation (see text). The energies of the inelastic peaks observed in $EuPd_2Si_2$ and $EuNi_2P_2$ are taken from [10] and [11], respectively. The corresponding values for the Eu valence are taken from [38] and [39].

At larger Ge content, Ex1 and Ex2 further shift in energy, lose intensity, and broaden. Interestingly, for $x = 0.75$, the QE signal seems to exist already at the lowest experimental temperature $T = 5$ K. For $x = 0.6$, the inelastic signal—if it still exists—practically disappears from the experimentally accessible energy window: assuming the same tendency observed in Si-rich compounds to still hold, the magnetic intensity should be concentrated mainly below 10 meV, as suggested by figure 6(a) for the lowest experimental temperature. At higher temperature, the magnetic response of the $x = 0.6$ compound seems to consist of a relatively narrow QE signal. Because of limitations in the accessible energy window (resolution of 3.7 meV, FWHM), the present experiment can provide only an upper limit (about 7.5 meV) for the linewidth of that signal. Therefore this composition should be studied in a separate experiment with higher resolution.

The energies of the inelastic peaks Ex1 and Ex2 for samples with different compositions and at different temperatures are plotted in figure 7 as a function of the Eu valence.

4. Discussion

In section 3, the magnetic excitation spectrum measured in $EuCu_2Si_2$ at 6 K was shown to exhibit no inelastic peak at the energy of 46 meV expected for the ionic $^7F_0 \rightarrow ^7F_1$ spin–orbit (SO) transition in Eu^{3+}, despite a valence of about 2.85. Instead, a double-peak structure, Ex1 and Ex2, occurs between 35 and 40 meV. The value of the cross-section associated with Ex2, as well as its Q

dependence following the Eu^{3+} magnetic dipole form factor, strongly suggest that it corresponds to the SO transition shifted to a lower energy. Such a shift was previously observed in $\mathrm{EuPd_2Si_2}$ [10], but not in the Sm-based IV systems $\mathrm{SmB_6}$ and (Sm, Y)S (gold phase), whose corresponding intermultiplet transitions occur close to the nominal ionic value[10]of 36 meV [4, 5]. The latter materials, however, are categorized as 'IV semiconductors' in reference to their low-temperature properties, whereas $\mathrm{EuM_2X_2}$ compounds have metallic ground states. A significant renormalization of the SO transition energies was shown to occur in several metallic Ce-based compounds [29–31], and ascribed to interactions with conduction electrons. A similar interpretation likely applies to the present case as well.

Within this scheme, it could be tempting to ascribe the double-peak structure to a crystal-field (CF) splitting of the excited $^7\mathrm{F}_1$ state. Eu sites have a tetragonal symmetry and the triplet $^7\mathrm{F}_1$ should split[11] into a singlet and a doublet [32]. A rough estimate can be obtained using CF parameters experimentally determined for the $\mathrm{RCu_2Si_2}$ series (R = Pr, Nd, Ho, Er) [33, 34]. Assuming those for $\mathrm{EuCu_2Si_2}$ to have a similar magnitude, the splitting of the $^7\mathrm{F}_1$ triplet should be in the range of 1–10 meV, which is comparable with the offset between Ex1 and Ex2. However the experimental intensity ratio (reduced to $Q = 0$) is Ex1:Ex2 ≈ 2:3, rather than 1:2 expected for transitions from the $^7\mathrm{F}_0$ singlet to the CF-split singlet and doublet substates of $^7\mathrm{F}_1$, respectively. Furthermore, taking into account the deviation of europium valence from 3+, the magnetic intensity derived for Ex2 *alone* already accounts for nearly the total cross-section calculated for the $^7\mathrm{F}_0 \rightarrow {}^7\mathrm{F}_1$ transition. This, together with the anomalous Q-dependence of its intensity, suggests that a different origin must be sought for Ex1.

In the following, we explore the possibility that the IV model previously suggested for the Sm-based IV systems (Sm, Y)S and $\mathrm{SmB_6}$ [35–37] could apply to the present compound. In that model, the ground state of IV samarium ions is argued to be a singlet of the same angular symmetry as the parent $^7\mathrm{F}_0$ state of Sm^{2+}. In particular, the magnetic excitation spectra observed experimentally in $\mathrm{SmB_6}$ were successfully interpreted in terms of (i) intermultiplet transitions from the parent Sm^{2+} and Sm^{3+} configurations, with significant damping reflecting their lifetimes, and (ii) a sharp exciton-like mode from the IV singlet ground state [4–6]. Since Eu^{3+} has the same electronic configuration as Sm^{2+}, IV europium can be considered a 'hole analogue' of Sm: the delocalization of one 4f hole occurs when the Eu valence changes from 3+ to 2+ (one *electron* delocalizes when Sm^{2+} goes to Sm^{3+}). In this approach, Ex1 and Ex2 could represent the spectral components associated with (ii) and (i), respectively, whereas the QE signal would originate from fluctuations within the Eu^{2+} state.

The fact that the QE scattering appears to vanish at low temperature in $\mathrm{EuCu_2Si_2}$ is an important issue. This can basically occur if the signal becomes either very narrow or strongly overdamped, or if the spectral weight is transferred to a different energy range, resulting in a spin-gap opening. A broadening of the QE peak as temperature goes down is physically plausible, because the lifetime of the Eu^{2+} partial configuration may become shorter when Eu changes to more trivalent. However, this explanation is unlikely since, in the whole temperature range where the QE peak is observed, its width remains rather large and almost temperature independent. The second explanation is even less probable because a narrowing of the QE signal with decreasing temperature has no physical ground in the present system. The most reasonable interpretation is therefore the opening of a spin gap, accompanying the formation of a singlet ground state, which would be is a natural consequence of the excitonic model of IV. A similar behaviour was reported previously for the Sm-based IV compounds (Sm, Y)S and $\mathrm{SmB_6}$ [4, 6]. It is interesting to note, in this connection, that the temperature of 100 K above which the QE signal appears on heating also corresponds to a change in the slope of the energy shift of Ex1 shown in figure 5(a). This may correspond to the onset of suppression of the in-gap excitonic-like mode (Ex1) by thermal fluctuations, as was previously observed in $\mathrm{SmB_6}$. In the solid solutions, the general behaviour of the QE signal for $x = 0.90$ is qualitatively similar to that of pure $\mathrm{EuCu_2Si_2}$. For $x = 0.75$ we observed a narrowing of the peak, from 23 meV (FWHM) at 200 K for $x = 1.0$ to about 8 meV and, for $x = 0.60$ most of the signal cannot be resolved with the present experimental condition. A detailed investigation of this behaviour will be performed in forthcoming experiments with higher resolution.

The similarity between the present situation and that encountered in Sm compounds is further substantiated by the response of the magnetic excitation spectrum to a change in the valence. In the (Sm, La/Ba/Ca)$\mathrm{B_6}$ series [7, 8] the valence can be varied in the range of 2.7–2.2. Correspondingly, the energy of the exciton-like mode decreases towards zero for $v \sim 2.7$, and extrapolates to the Sm^{2+} ionic SO energy of 36 meV as v approaches 2+. In the excitonic model for Sm-based systems [37], the energy Δ^*_{SO} of the exciton-like peak (corresponding to a SO excitation within the extended part of the IV singlet ground state wavefunction) can be derived from the SO transition energy in the parent Sm^{2+} state. The energy shift scales with the valence change according to the formula:

$$\Delta^*_{\mathrm{SO}} = (3 - v)\Delta^{\mathrm{Sm}^{2+}}_{\mathrm{SO}}, \tag{1}$$

which becomes, for IV europium compounds

$$\Delta^*_{\mathrm{SO}} = (v - 2)\Delta^{\mathrm{Eu}^{3+}}_{\mathrm{SO}}. \tag{2}$$

But whereas, in Sm hexaborides, the energy of the SO transition associated with the Sm^{2+} parent state, $\Delta^{\mathrm{Sm}^{2+}}_{\mathrm{SO}}$, remained unchanged across the series, that of Ex2, ascribed to Eu^{3+} in the $\mathrm{EuCu_2(Si_xGe_{1-x})_2}$ series, varies almost linearly with the valence state (solid line in figure 5). As mentioned

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[10] The same scheme of SO transitions is expected in Sm^{2+} and Eu^{3+} ions, but with different energies: 36 meV and 46 meV, respectively, for $^7\mathrm{F}_0 \rightarrow {}^7\mathrm{F}_1$.

[11] This leaves aside the question of whether such a CF splitting would be observable if the characteristic energy of valence fluctuations (estimated from the experimental width of the quasielastic response to be larger than 10 meV) exceeds the CF energy.

above for pure $EuCu_2Si_2$, this dependence is thought to reflect the role of conduction electrons in the formation of the IV state. Using it as an experimental estimate of $\Delta_{SO}^{Eu^{3+}}$ as a function of the valence state, one can use equation (2) to derive the variation of Δ_{SO}^{*}, which is plotted as a dashed line in figure 7. One sees that the agreement with the energy of Ex1 is fairly good. It is also interesting to note, in figure 7, that the energy of Ex2 itself extrapolates linearly to the ionic SO transition energy of Eu^{3+} (46 meV) for $\nu \rightarrow 3$.

The comparison can be extended to another member of the EuM_2Si_2 family, $EuPd_2Si_2$, previously studied by Holland-Moritz *et al* [10]. In that compound, the only excitation reported was the Eu^{3+} (renormalized) SO transition, corresponding to Ex2 in the notations of this paper. The corresponding data points, plotted in figure 7, are in good agreement with the general dependence observed in $EuCu_2(Si_xGe_{1-x})_2$. The lack of observation of the lower mode Ex1 may be due to the valence being closer to 3+. Actually, some faint indication of the presence of Ex1 in $EuPd_2Si_2$ may exist in the spectrum measured at $T = 120$ K in [10]. Also plotted in figure 7 are the data for $EuNi_2P_2$ from [11]. In that compound, the valence is closer to 2+, and only one peak is observed. Its energy is quite low, less than 10 meV, which is roughly in the range expected for Ex1 according to the dependence found in silicides. However, the possibility of a stronger renormalization of Ex2 cannot be ruled out.

Let us turn now to the Q dependence of Ex1 intensity. In Sm-based systems, the Q dependence of intensity of an excitonic-like peak was systematically observed to be steeper than the calculated dipole form factor for the $^7F_0 \rightarrow {}^7F_1$ SO transition. This was consistent with the idea that the magnetic f-electron density in IV state is more delocalized than that of the original Sm^{2+} orbital, implying that the corresponding form factor should have lesser extension in Q space. In $EuCu_2Si_2$ the opposite effect is observed experimentally.

To try to understand this puzzling result, we first recall that the form factor for the intermultiplet SO transition can be written [40] (limiting to second order, for argument's sake) as the difference:

$$F = \langle j_0 \rangle - \langle j_2 \rangle, \qquad (3)$$

between the integrals $\langle j_0 \rangle$ and $\langle j_2 \rangle$, reflecting the radial distribution of electron spin and orbital magnetic moment density. The possibility therefore exists that, although the dependence of each term taken separately becomes steeper, their difference may decrease more slowly, at least in the Q range accessible experimentally if the change is more pronounced for $\langle j_2 \rangle$ than for $\langle j_0 \rangle$. Furthermore, if the observed transition arises from a more extended electron state than the original atomic 4f orbital, the balance between the spin and orbital component may be altered, an extreme example of such a situation being the complete quenching of d-electron orbital moments in transition elements. A quantitative calculation of the Q dependence of the scattering cross-section within the excitonic IV model is beyond the scope of this paper. We shall only note here that the experimental dependence for Ex1 plotted in figure 4 corresponds fairly well to that calculated for the $\langle j_0 \rangle$ integral alone.

5. Conclusion

In this work we have presented a detailed inelastic neutron scattering study of the spin dynamics in intermediate valence Si-rich $EuCu_2(Si_xGe_{1-x})_2$ solid solutions. For $x = 1$, the magnetic excitation spectrum was found to consist of a double-peak structure just below the energy range of the Eu^{3+} $^7F_0 \rightarrow {}^7F_1$ spin–orbit excitation, whose higher-energy spectral component can be assigned to the renormalized spin–orbit transition. The change in the Eu valence towards 2+ with increasing temperature or Ge concentration results in a further renormalization to lower energies, and gradual suppression, of both inelastic peaks in the spectrum, while a sizeable quasielastic signal develops. A simple phenomenological description of the results, also including data from earlier works on other materials from the same Eu-based family, is suggested in terms of the excitonic model of intermediate valence previously elaborated for the Sm-based systems SmB_6 and (Sm, Y)S. In contrast to the latter mixed valence semiconductors[12], $EuCu_2(Si_xGe_{1-x})_2$ are metals, which raises the question of whether a common approach may be applicable to both situations. Indeed, the existence of exciton-like magnetic modes, associated with a spin-gap opening in the magnetic excitation spectrum, has recently been discussed for such different materials as cuprate and ferropnictides superconductors or antiferromagnetic CeB_6 (both metallic), as well as for the Kondo insulator YbB_{12}. It would be premature to propose a unifying framework for those phenomena but further studies of this topic are clearly desirable. In the present series of compounds, the concentration range around $x = 0.6$, for which a coexistence of magnetic order and valence fluctuations has been reported, is of particular interest and should be studied with higher experimental resolution.

Acknowledgments

We are grateful to I P Sadikov, N V Znamenskiy, C Geibel, A V Kuznetsov, E S Clementyev, J Röhler, Yu Kagan, E A Goremychkin and Th Brückel for stimulating discussions, to J Taylor for his support during the INS experiment, and to J de Groot and B Schmitz for their help in the magnetic test of the sample quality. Authors PAA, J-MM, KSN are grateful to the ISIS facility for hospitality during the experiments.

The work was supported by the RFBR grant No. 11-02-00121.

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[12] In reality, this applies only to the pure parent compounds, while the magnetic spectral features of interest here survive at least partly in the metallic state in solid solutions.

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